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Preliminary background ozone concentrations in the mountain and coastal areas of Bulgaria

E. Donev[a], K. Zeller[b,*], A. Avramov[a]

[a]*Department of Meteorology, Faculty of Physics, Sofia University, Bulgaria*
[b]*USDA Forest Service, Rocky Mountain Research Station, 240 W. Prospect, Fort Collins, CO 80526, USA*

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"Capsule": *Rural forested, mountain regions of Bulgaria experience average ozone concentrations in excess of 40 ppb, slightly exceeding the 10000 ppb hour critical European daytime AOT40 level.*

Abstract

Urban and non-urban rural ozone (O_3) concentrations are high in Bulgaria and often exceed the European AOT40 ecosystem as well as the AOT60 human health standards. This paper presents preliminary estimates to establish background, non-urban O_3 concentrations for the southern region of Bulgaria. Ozone concentrations from three distinctly different sites are presented: a mountain site influenced by mountain–valley wind flow; a coastal site influenced by sea-breeze wind flow; and a 1700-m mountain peak site without 'local' wind flow characteristics. The latter offers the best estimate of 46–50 ppb for a background O_3 level. The highest non-urban hourly value, 118 ppb, was measured at the mountain-valley site. © 2002 Published by Elsevier Science Ltd.

Keywords: Ozone; Rural air quality; Background concentrations; Meteorology; AOT40

1. Introduction

Routine measurements of Bulgarian non-urban ambient ozone, O_3, are not available. Limited data indicate that O_3 is a serious problem in southern Europe where the climate is favorable for O_3 formation (Pleijel, 2000). Maximum urban O_3 in Bulgaria during summer 2000 were higher than any other eastern European country: 212 and 248 ppb for May and June, respectively (Phare Topic Link, 2000). Hourly O_3 levels often exceed 100 ppb in the Mediterranean region, especially in Greece on Bulgaria's south southwestern border (Güsten et al., 1988; Danalatos & Glavas, 1996). The World Health Organization (1997) has found increasing NO_2 (an O_3 precursor) in the ambient air of Sofia, Plovdiv and other cities. It is well known that tropospheric O_3 is generated downwind of such cities, hence a knowledge of non-urban background O_3 is needed in Bulgaria.

Bulgarian measurements of non-urban O_3 started in 1994 at the Ovnarsko (Fig. 1) climatology site located within the Govedartsi Valley on the northwest slope of Rila Mountain in southwest Bulgaria (Donev et al. 1996, 1998, 1999; Zeller et al., 1996, 1997). The Ovnarsko measurements distinguished O_3 behavior during periods affected by various *synoptic* conditions from periods affected by *local* mountain–valley wind flows. These two wind regimes impact diel O_3 concentration patterns as discussed by Donev et al. (1996). A second mountain monitoring site, Rojen (Fig. 1), was initiated in October 1998 on a gentle peak in the Rhodopa Mountains in south central Bulgaria. This site was selected to contrast the Ovnarsko site with a moderate elevation, mountain site not influenced by local orographic wind flows. In June 1999 the Ovnarsko site monitoring equipment was moved to Ahtopol (Fig. 1), a coastal site in southeast Bulgaria close to Turkey, to compare Rojen O_3 behavior with a remote coastal site, influenced by land-sea wind flows. The west to east transect of these three sites provides a first evaluation of rural background O_3 in this southern Bulgaria region. All three sites are far from densely populated and industrial areas.

* Corresponding author. Tel.: +1-970-498-1238; fax: +1-970-498-1212.

E-mail address: k.zeller@lamar.colostate.edu (K. Zeller).

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Fig. 1. Location of Ovnarsko, Rojen and Ahtopol monitoring sites in Bulgaria.

This paper presents rural O_3 concentrations and provides insight as to how O_3 patterns differ between mountains and seacoast. This information also helps identify O_3 risk to remote forests. Such parallel measurements of O_3 are made for the first time in Bulgaria.

2. Methods

2.1. Site descriptions and measurements

The Ovnarsko site, Fig. 1, (latitude 42° 20′ N, longitude 23° 22′ E) is situated 1600 m above sea level (a.s.l.) in the northwestern part of Rila Mountain (Zeller et al. 1992, 1997; Donev et al. 1996, 1998, 1999), the highest mountain on the Balkan Peninsula. The site is fully described by Zeller et al. (1997). The closest anthropogenic pollution sources are about 30 km to the west, blocked by surrounding mountain ridges.

The Rojen site, Fig. 1, (Lat. 41° 40′ N; Lon. 24° 48′ E) is situated at 1700 m a.s.l. in the central part of Rhodopa mountains. The Rojen site is approximately 250 km east from Ovnarsko site and about 100 km south of the nearest industrial activity. It is situated on a gentle-sloped mountain peak in a forest opening 2–3 m above the surrounding treetops.

The Ahtopol site, Fig. 1, (latitude 41° 58′ N, longitude 27° 57′ E) at 20 m ASL is surrounded by grass vegetation and situated in the south-east part of Bulgaria about 200 m west of the Black Sea shoreline and 200–300 m east of a forest edge. The site is 2 km to the south of the small town Ahtopol. In this area the Strandzha Mountains extend to the Black Sea from the west. Prior to 1991, the Ahtopol site was a Bulgarian–Russian cooperative meteorology rocket facility closed to the public for 40 years.

2.2. Basic measurements

At Ovnarsko, wind speed, direction and vertical wind speed sensors were located at 10-m height; air temperature and humidity, solar radiation, pseudo-wetness sensors were located at 2 m height. Precipitation, soil temperature and soil heat flux were also measured. The Ovnarsko and Ahtopol equipment is explained by Donev et al. (1996) and Zeller et al. (1997). Ozone was sampled at 2 m at Ovnarsko and 1 m at Ahtopol. The ozone instrument, a TECO 49, internally adjusts for temperature and pressure. It was calibrated in the USA before shipment to Bulgaria in 1996. Another calibration was made in 1998 by the Bulgarian National Center of Environment and Sustainable Development under the Ministry of Environment using the Bulgarian primary standard. Calibration results showed that there had been no drift in the output signal. Previous Ovnarsko O_3 measurements, limited to early summer months, revealed no high O_3 episodes; hourly O_3 concentrations ranged from 20 to 70 ppb (Donev et al. 1996, 1998, 1999). However, the data presented here demonstrate that ozone episodes do occur at Ovnarsko (see detailed topography map in Donev et al., 1996).

The basic meteorological parameters measured at Rojen were wind speed and direction, temperature and relative humidity, precipitation and solar radiation. Ozone measurements (sample inlet: 1 m height) commenced in October 1998 employing a Dasibi UV-analyzer provided by the National Center of Environment and Sustainable Development. It was calibrated in 1998 at the same center using the Bulgarian primary standard. Due to the inherent stability of the UV adsorption technique and applying the calibration results, the accuracy of the ozone measurements reported here is ±3 ppb.

3. Results and discussion

3.1. Daily average ozone concentration

Fig. 2a and b give the daily average (i.e. 24-h mean) O_3 concentration for two simultaneous sampling periods: (1) Ovnarsko and Rojen from 22 October 1998 to 26 June 1999; and (2) Rojen and Ahtopol from 6 July 1999 to 31 December1999.

Ovnarsko hourly O_3 concentrations (not plotted) rarely exceed 60 ppb during the day and drop 20–40 ppb at night. Relatively higher O_3 concentrations were measured during synoptic wind days when air from the southwest and west enters the valley (e.g. versus local wind days). There were three episodes of high O_3, $\geqslant 80$ ppb, hourly averages at Ovnarsko not previously experienced (Donev et al., 1996, 1998, 1999; Zeller et al. 1997). These occurred in April 1998, August 1998 and November 1998. Fig. 2a shows two >60 ppb 24-h peaks in November 1998 when the maximum 1-h concentration of 118 ppb occurred on 1 November 1998. This episode, the highest ever recorded at Ovnarsko, coincided with a sharp increase in air temperature followed by a west-southwest increase in wind speed. Simultaneously, the wind at Rojen was also from west-southwest, but the temperature did not increase and there was no ozone episode.

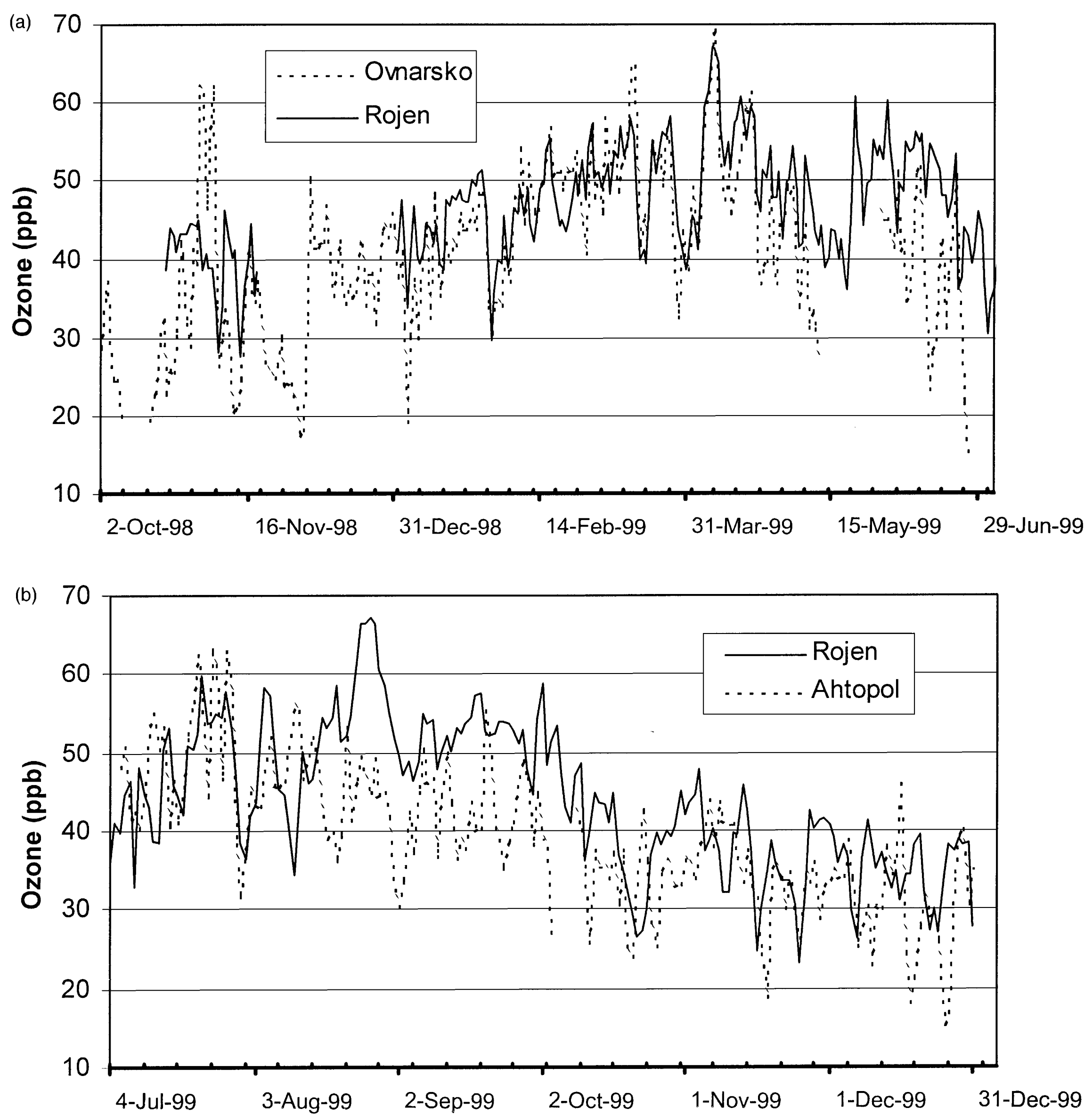

Fig. 2. (a) Daily 24-h O_3 concentration means (ppb) at Ovnarsko and Rojen from 22 October 1998 to 26 June 1999. (b) Daily 24-h O_3 concentration means (ppb) at Ahtopol and Rojen from 6 July 1999 through the end of 1999.

Daily average O_3 concentrations at Rojen generally track those at Ovnarsko and exceed those at Ahtopol (Fig. 2b). There were two 5-day periods of high 24-h concentrations (>60 ppb; Fig. 2a and b) during April and August when hourly values reached 75 ppb. During the April period, hourly Ovnarsko concentrations were even higher. The August O_3 episode at Rojen was not evident at Ahtopol. Local flows (i.e. mountain–valley and land–sea) known to help scavenge O_3, lowering O_3 concentrations (Broder and Gydax, 1985; Zeller, 1995; Donev et al., 1996) may account for the lower Ahtopol levels. These comparisons lead the authors to believe that Rojen provides representative background O_3 measurements for southern Bulgaria.

3.2. Critical levels of ozone

The 'accumulated O_3 exposure over a concentration threshold of 40 ppb during daylight hours:' AOT40 index, calculated for either a 3 or 6 month growing season (Skarby and Karlsson, 1996; Fuhrer, 2000), is the European standard alerting for potential ecosystem impact. Some authors report 'full day' AOT40 values (Skarby and Karlsson, 1996). The critical daytime AOT40 value for trees over a 6-month growing season is 10 000 ppb-h. For acute effects, like visible damage, the standard is 500 ppb-h during 5 consecutive days with VDP >1.5 kPa (vapor pressure deficit) or 200 ppb-h for 5 days with VPD <1.5 kPa. AOT60 values (accumulated exposure over a concentration threshold of 60 ppb) are similarly used for indicating O_3 levels sufficient to harm health (Skarby and Karlsson, 1996).

1999 Rojen AOT40 results (Table 1) are several times above the 'acute' level for the two 5-day episodes: 6–10 April and 24–28 August 1999. The calculated AOT60 values for these two periods also indicate levels sufficient to harm human health. Although the AOT40 and AOT60 levels were high, maximum 1-h average values never exceeded 75 ppb. Average O_3 concentrations during these two periods, 58 and 66 ppb, exceed the overall averages 46–50 ppb. The latter concentrations provide a starting point for establishing a background value for southern Bulgaria.

3.3. Diurnal variations of ozone concentrations

Mueller (1994) has shown that diel O_3 amplitudes diminish with elevation at rural mountain sites. There is also a tendency for multi-hour phase shifts in the diel O_3 cycle: maximum values are measured during the night (Aneja and Li, 1992, Zeller, 1995) as recorded for Rojen (Fig. 3). This is not the case for Ovnarsko and Ahtopol where both are influenced by local flows: mountain–valley and coastal sea breeze circulation, respectively (Prevot et al., 1993). Fig. 3. shows the combined (synoptic and local) diel concentration cycle at all sites.

Table 2 gives the overall daily average statistics for local, non-local and all days for the comparison periods in Fig. 2. Ozone cycles during local wind flow periods experience greater diel amplitudes (e.g. concentrations are lower at night and higher during daylight). Ahtopol's O_3 concentrations are generally lower and its maximum–minimum amplitudes higher than both Rojen and Ovnarsko. Rojen average concentrations are always higher than the other sites. Interestingly, local days give higher averages for all sites, with Rojen's averages the highest. The Rojen 24-h average maximums and minimums are either lower (during maximum) or higher (during minimum) than the other two sites.

4. Conclusion

The analysis of O_3 at three very different remote sites has demonstrated the impact of local geography and associated wind flows on concentrations. Compared to Rojen, the mountain top site, Ahtopol, the seacoast site, has overall lower O_3 concentrations and Ovnarsko, the mountain-valley site, experiences higher hourly concentrations. Rojen appears to be the best site for estimating background O_3 concentration values for

Table 1
Critical levels: AOT40 and AOT60 for O_3 at Rojen during 1999

Period	Maximum O_3 (ppb)	Average O_3 (ppb)	AOT40 (ppb h; Solar rad. > 50 W m^{-2})	AOT40 (ppb h; Solar rad. > 50 W m^{-2} and VPD[a] < 1.5 kPa)	AOT40 (ppb h; full 24 h day)	AOT60 (ppb h; Solar rad. > 50 W m^{-2})	AOT60 (ppb h; full 24 h day)
all 1999	75	46	28 045	27 403	68 504	764	2191
April–September	75	50	20 277	19 662	45 966	723	2107
May–July	71	47	8106	7989	17 976	80	366
6–10 April	75	58	1494	1494	3210	187	530
24–28 August	75	66	1587	1587	3074	387	732
8 July–20 October[b]	75	50	10 474	9921	26303	460	1222

[a] Vapor pressure deficit
[b] July–October values for comparison see Zeller (this issue).

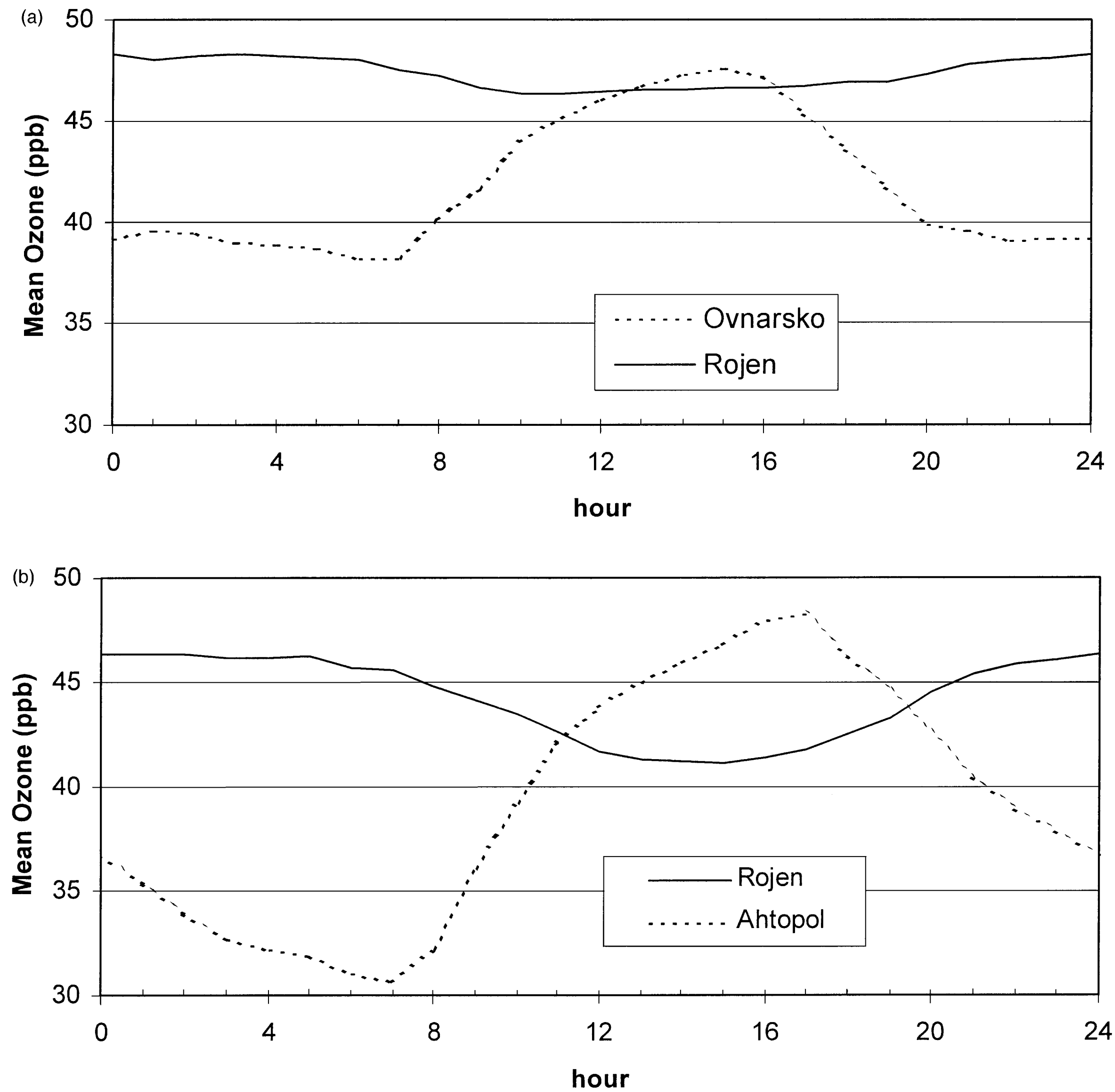

Fig. 3. (a) Diel O_3 concentration cycle (ppb) at Ovnarsko and Rojen from 22 October 1998 to 26 June 1999. (b) Diel O_3 concentration cycle (ppb) at Ahtopol and Rojen from 6 July 1999 to the end of 1999.

Table 2
Average daily 24-h ozone (ppb) variations for local, non-local and all days during the two analysis periods including the maximum 1-hour (ppb) values

No. of local days	Period 1: 22 October 1998–26 June 1999	Local wind days (ppb)				Non-local wind days (ppb)				All days (ppb)				
	Period 2: 6 July 1999–31 December 1999	Avg.	Max.	Min	Ampl.	Avg.	Max.	Min	Ampl.	Avg.	Max.	Min	Ampl.	Max 1-h
95	Rojen (1+2)	50.2	53.1	47.2	5.8	44.2	45.7	42.6	3.0	45.7	47.2	43.8	3.4	75
39	Rojen (1)	51.3	53.2	50.0	3.2	46.4	47.6	45.3	2.3	47.3	48.3	46.4	1.9	75
56	Rojen (2)	49.1	52.9	44.2	8.7	42.0	43.9	39.6	4.3	44.2	46.4	41.1	5.3	75
39	Ovnarsko (1)	45.1	54.1	39.0	15.1	41.2	46.3	37.8	8.5	41.9	47.6	38.2	9.5	118
56	Ahtopol (2)	41.0	54.4	26.8	27.6	38.5	45.6	32.5	13.1	39.3	48.2	30.7	17.5	89.5

southern Bulgaria: 46–50 ppb. These values imply that the AOT40 O_3 level maybe exceeded as a background value! The results for two 5-day periods demonstrate exceedences above the acute level for causing visible damages. AOT60 values also indicate a potential risk to human health. This is the first time such an analysis has been made for Bulgaria. It is clear that there is more work to be accomplished for both reducing O_3 levels and for making these results available to governmental decision makers.

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